1. Introduction

Antioxidants are one of the most important components among the additives to the fuels and lubricants. For example, dithiophosphates and dithiocarbonates of metals (mainly zinc dithiophosphate), secondary aromatic amines (N-phenyl-α- and β-naphthylamines, N,N-dietylphenylamine), hindered alklyphenols, etc. have obtained the broadest practical application in the lubercants. Alkylsalicylates of the alkaline-earth metals also have good antioxidative and anticorrosive properties in the fuels and lubricants.

Extensive synthetic investigations in the 1930s have led to the creation of the antioxidants that are valuable even today. It was found that hindered alklyphenols are the most effective among phenolic antioxidants. All contemporary chemistry of the phenolic antioxidants is based on them. Even today various derivatives of the 2- or 2,6-di-tert-Butlyphenol are successfully used in this sphere. Each of these types of antioxidants has some advantages as well as disadvantages.

Hindered phenols and secondary aromatic amines have an advantage because they are almost ashless additives. But they do not protect metal surface from corrosion. Aromatic amines in comparison with the hindered phenols are more toxic and, in addition, they are able to color lubricants during the oxidation process. At the relatively low temperatures, 4-methyl-2,6-di-tert-Butlyphenol (Ionol) is one of the most effective hindered alklyphenols. It is a unique component of the additives in the breadth of its application because in the second half of the 20th century it has been already used in the global market by more than 70 trademarks. However, Ionol has a high volatility that is a significant disadvantage.

Thus, synthesis of the effective ashless high-temperature additives to the fuels and lubricants is urgent today.
2. Analysis of the literature sources and problem statement

One of the most common classes of the antioxidants are phenol derivatives [1] that may also contain alkyl groups that screen hydroxyl group, thereby increasing the oxidant capacity of additives. However, their usage is limited because of the insufficient thermal stability. For example, adding of 0.5 % of the di-tert-Butylhydroquinone significantly improves the stability of the biodiesel, but, as it has been shown by the analysis of the oxidation induction period by the ASTM D-6751 method, the necessary degree of the stability has not been achieved [2]. Zine dithiophosphates have quite high antioxidant effectiveness [3, 4]. However, the usage of these antioxidants in the fuels is limited because they are ashy. In addition, they are not enough thermally stable and reduce the colloidal stability of the lubricants.

Alkylsalicylate derivatives of the metals are more stable [5], but they also belong to the ashy additives. Decomposing at the high temperatures, for example, in the area of the engine piston rings while being used in the motor oils they participate in the formation of the deposits. Ash is also an obstacle for the nanomaterials usage in the fuels and lubricants, in particular, zeolites, which also have the ability to increase resistance of hydrocarbons to oxidation [6].

Hindered alkylphenol Mannich bases also deserve attention [7–9]. In particular, N-benzyl-N,N-bis-(3,5-di-tert-Butyl-4-hydroxybenzyl)-amine is an effective inhibitor of the complex lithium lubricants oxidation [8]. It is reasonable to use it in the high-temperature lubricants. Alkylphenol Mannich bases are actively researched and patented not only as components of the lubricants but also as additives to the fuels [10]. The usage of the Mannich reaction for the industrial products synthesis is considered as perspective because it is rather simple and technically “convenient” and can be easily implemented in practice. It is also characterized by minimal waste formation.

Derivatives of the 1,3,5-triazine are also interesting additives among the high-temperature antioxidants of the organic compounds [11, 12]. 1,3,5-Tris-(3,5-di-tert-Butyl-4-hydroxybenzyl)-isocyanurate (trade marks Good-Rite 3114, Irganox 3114) is thermally stable up to 300 °C (it loses 7 % of the weight) and tris-(3,5-di-tert-Butyl-4-hydroxybenzyl)triazine (TTS) loses 7.5 % of the weight up to 250 °C. Antioxidant activity of the hindered alkylphenol derivatives of the sym-triazine depends also on the origin of the groups that connect triazine ring with the phenolic fragment. The substances in which 1,3,5-triazine is connected with the hindered alkylphenol by sulfur, i.e. compounds of the TTS-type, have the highest antioxidant activity [11].

Trithiocyanuric acid (TTCA) is a good reagent for the synthesis of the sulfuric alkylphenol derivatives of the sym-triazine. Synthesis of the compounds based on the TTCA with paraformaldehyde and alkylphenols is quite simple. However, there are some problems during TTCA synthesis from 2,4,6-trichlorotriazine by the reaction with thiocarbamido or Na2S and NaHS [13].

Along with the rather low output TTCA can be synthesized by the trimerization of the thiocyanic acid [14]. As a raw material to the TTCA synthesis, the 2,4,6-trichlorotriazine is used. It is commercially produced by trimerization of the cyanogen chloride with hydrogen chloride addition; and it is widely used in the colorants, insecticides, herbicides and medicine production. However, it is quite toxic. And this fact stimulates the search of the less toxic and more environmentally safe reagents for the synthesis of the compounds that have similar structure to the tris-(alkyl-oxymethyl)triazines and provide high antioxidative activity, availability of the raw materials, simplicity of the synthesis, thermal stability, low volatility, and multifunctionality.

One of the available raw materials for the synthesis of the additives to the lubricants is ammonium thiocyanate that during fusion with the hydrosulfates of the alkaline metals or ammonium forms the mixture of the TTCA (~10 %) and the thiocyanic acid polymer (N=N−SH)n (~60 %) [15]; and with the sulfuric acid – 5-amino-1,2,4-dithiazole-3-thione (Xanthane Hydride) [16].

Earlier it was reported [17, 18], that the thiocyanic acid polymer and 5-amino-1,2,4-dithiazole-3-thione react with paraformaldehyde and alkylphenols and form products that show multifunctional properties in the oils. Consequently, the usage of the available raw material – ammonium thiocyanate – for the synthesis of the new perspective additives to fuels and lubricants is urgent and requires more detailed study of their functional properties and structure.

3. Research aim and tasks

The aim of the investigation is to obtain highly efficient and thermally stable additives to the fuels and lubricants. For ensuring reliable operation of the mechanisms, these products have to be ashless, maintain antioxidative properties at the temperatures above 200 °C and contain heteroatoms and cyclic fragments that are able to provide multifunctional properties in the oils and motor fuels.

To achieve the aim of the research, the following tasks were set:

- synthesis of the alkylphenol derivatives of the thiocyanic acid polymer and 5-amino-1,2,4-dithiazole-3-thione (Xanthane Hydride);
- determination of the functional properties of the synthesized additives in the oils;
- optimization of the method of the Xanthane Hydride synthesis and structure determination of the products of its condensation with paraformaldehyde and 2,6-di-tert-Butylphenol (2,6-DTB).

4. The results of the research of the properties of the additives to the fuels and lubricants and their discussion

4.1. Alkylphenol derivatives of the thiocyanic acid polymer

Thiocyanic acid polymer (−C(SH)=N−C(SH)=−N−C(SH)=N−)n that is synthesized by the reaction of the ammonium thiocyanate with the anhydrous NaHSO3 [15] can be considered as the linear analogue of the TTCA. The molecular mass of the polymer, determined by the ebulliometric method in the pyridine, is ~6000.

Thiocyanic acid polymer was synthesized in this way. The mixture of 7.6 g (0.1 mole) of NH4SCN and 30.2 g (0.25 mole) of anhydrous NaHSO3 was heated approximately 30 minutes at the temperature of the 140 °C. After it was cooled to the room temperature, the double amount of water (in relation to the initial reagents) was added, the mixture was carefully blended. Then the precipitate was filtered and drying. After the precipitate drying 4.5 g (76 %) of the aim product was obtained. It consists mainly of the polymer (HSCN)n (~60 %)
According to the results of the experiment, they have multifunctional properties in the oils, similar to the tris-(hydroxybenzylthio)-triazinate and also are not inferior in the thermal stability (according to the derivategravimetric investigations 10 % of the mass is lost in the temperature range 240–256 °C depending on the nature and structure of alkylphenol). Antioxidative and anticorrosive properties of these compounds are a bit higher than the similar properties of the bis-(4-hydroxy-3,5-di-tert-Butylbenzyl)sulfide. Antioxidative properties of the compounds were determined by the method of the oxygen absorption in the solution of the vaseline oil (200 °C) at the atmospheric pressure at the bubble type facility with automatic compensation of the absorbed oxygen [20].

4. 2. Alkylphenol derivatives of 5-amino-1,2,4-dithiazole-3-thione (Xanthane Hydride)

4. 2. 1. Synthesis of 5-amino-1,2,4-dithiazole-3-thione

A convenient laboratory method of the 5-amino-1,2,4-dithiazole-3-thione synthesis by treating an aqueous solution of the ammonium thiocyanate with the sulfuric acid is in detail described in the literature [16]. The output of the aim product (Xanthane Hydride) by the reaction (1) is approximately 68 %.

$$6\text{NH}_4\text{SCN} + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{N} \cdot \text{C} = \text{C} = \text{S}^+ + 3(\text{NH}_4)_2\text{SO}_4 + 2\text{HCN}. \quad (1)$$

It was found that instead of the sulfuric acid it is better to use hydrochloric acid. The output of the aim product does not decrease and it can be easier purified to the analytically pure grade. In addition, the usage of the sulfuric acid leads to the formation of approximately 1 % of toxic hydrogen cyanide from the amount produced according to the reaction equation. When hydrochloric acid is used, not more than 0.2 % of the hydrogen cyanide from the amount calculated according to the reaction equation is released into the atmosphere. So, one can see that it is better to synthesize 5-amino-1,2,4-dithiazole-3-thione by treating an aqueous solution of the ammonium thiocyanate with the concentrated hydrochloric acid in equimolar proportions at the temperature range of 5–15 °C.

To the solution of the 200 g (2.6 mole) of the ammonium thiocyanate ("pure" grade) in the 150 ml of water during the stirring and cooling to the temperature of (5±2) °C the 200 ml of the hydrochloric acid (37 % concentration) were added dropwise during 2 hours. The mixture was kept during the stirring at the temperature of 5–15 °C for 5 hours. Then it was left for 12 hours at the temperature of (20±2) °C. The yellow precipitate was filtered, washed with water and dried in the vacuum desiccator over the phosphoric anhydride. The aim product (5-amino-1,2,4-dithiazole-3-thione) output is 68–72 %.

For analysis, the product was purified by recrystallization from an aqueous solution of the dimethylformamide. Decomposition tempera-
ture is 205 °C. The following elemental composition was found, %: S – 63.7, N – 18.0. For the empirical chemical formula of the 5-amino-1,2,4-dithiazole-3-thione C₂H₂N₂S₃, the calculated values of the chemical elements content are, %: S – 64.0, N – 18.6. It proves the correctness of the synthesis of the Xanthane Hydride.

In the Infrared spectrum of the 5-amino-1,2,4-dithiazole-3-thione (recorded by spectrometer “UR-20”) in the area of the 1500–1800 cm⁻¹ there are two wide intensive bands of the absorption – 1530 and 1640 cm⁻¹, that are caused by the group

\[ \text{N} = \text{C} \equiv \text{S} \]

The wide band in the area of the 2800–3300 cm⁻¹ with several weakly expressed peaks also corresponds to the associated N–H bonds. In the PMR spectrum [(CD₃)₂S=O] there are two close presssed peaks also corresponds to the associated N–H bonds.

An output of the unpurified 5-amino-1,2,4-dithiazole-3-thione decreases to 40 % during ammonium thiocyanate treatment with the hydrochloric acid at the temperature of the 20–25 °C. The content of the sulfur in the aim product also reduces notably – approximately by 5–6 % compared with a pure 5-amino-1,2,4-dithiazole-3-thione sample. The content of the nitrogen increases by 1–2 %. Therefore, the reaction of the ammonium thiocyanate with the hydrochloric acid has to be conducted with cooling to 5 °C to obtain the Xanthane Hydride of high quality.

Ammonium thiocyanate is dissolved in the concentrated sulfuric acid for the synthesis of the analytically pure compound; insoluble precipitate is filtered on a glass filter, clear solution is poured on the ice. Completely pure samples of the Xanthane Hydride can be also synthesized by the careful addition of water to its saturated solution in the dimethylformamide.

### 4.2.2. Condensation of the Xanthane Hydride with paraformaldehyde and 2,6-di-tert-Butylphenol (2,6-DTB)

Condensation was carried out in the glacial acetic acid at the temperature of 40–45 °C in the molar ratio of the reagents 5-amino-1,2,4-dithiazole-3-thione:paraformaldehyde:2,6-DTB = 1:6:2.7. These conditions are found as an optimal for increasing the product output.

The process was carried out as follows. To the solution of the 14 g (0.068 mole) of the 2,6-di-tert-Butylphenol in the 50 ml of the glacial acetic acid, the 3.8 g (0.025 mole) of the Xanthane Hydride and 4.5 g (0.15 mole) of the paraformaldehyde were added. The reaction mixture was agitated at the temperature of (40±2) °C for 2 hours and 1 hour at the temperature of (45±2) °C, and then it was left for 12 hours. Precipitate was filtered, washed three times with acetic acid (with 10 ml portions), and dried under the pressure of 133.3 Pa. So 15.6 g of the yellow solid product was synthesized. This product was three times treated with the boiling benzene (150 ml portions). Precipitate that was not dissolved in the benzene (8.9 g) is a more fine-crystalline product (1) and after washing with the acetonitrile and drying under the pressure of 133.3 Pa it has a melting temperature of 160–162 °C.

After the benzene evaporation, 6.7 g of the product (2) was synthesized in the form of the yellow crystalline substance with a melting temperature of 75–80 °C after the low-temperature crystallization from hexane.

A mixture of the products is obtained during the condensation. The material balance of this reaction (Table 2) shows that as a result of the reaction there is a precipitate, which is 70 % of the taken initial reagents. The precipitate that fell, represents a mixture of the products (1) and (2) that could be split by means of the boiling benzene in which the product (2) is well soluble. By the mass fraction, these products were 40 % for (1) and 30 % for (2) of the mass of the substances used for this reaction.

<table>
<thead>
<tr>
<th>№</th>
<th>Reagents</th>
<th>Mass, g</th>
<th>Amount of the compounds, mole</th>
<th>Product</th>
<th>Mass, g</th>
<th>Mass fraction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Xanthane Hydride</td>
<td>3.8</td>
<td>0.025</td>
<td>Precipitate, including</td>
<td>15.6</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>2,6-Di-tert-Butylphenol</td>
<td>14.0</td>
<td>0.068</td>
<td>The product insoluble in the benzene (1)</td>
<td>8.9</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>Paraformaldehyde</td>
<td>4.5</td>
<td>0.15</td>
<td>The product soluble in the benzene (2)</td>
<td>6.7</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Total:</td>
<td></td>
<td></td>
<td></td>
<td>22.3</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: The material balance of the condensation of the Xanthane Hydride with 2,6-di-tert-Butylphenol and paraformaldehyde

Compound (1) is a white fine-crystalline powder, for which the simplest empirical formula C₂₀H₂₇N₂O(3–4)S₃ was calculated by the average values of the elemental analysis (C – 49.4 %; H – 6.1 %, N – 6.0 %, S – 21.1 %). Its structural formula is shown in Fig. 1.

![Fig. 1. The chemical formulae of the product (1)](image)

Considering the low solubility of the product (1) in the organic solvents, it was assumed that Xanthane Hydride ring was not changed. However, the comparison of the Infrared spectrum of the Xanthane Hydride and product (1) shows that they differ noticeably in the area of the 1500–1800 and 2900–3500 cm⁻¹. Xanthane Hydride has two specific bands at the 1510 and 1640 cm⁻¹ which are noticeably shifted in the product (1) (1440 and 1605 cm⁻¹). This shows the movement of the multiple bonds in the Xanthane Hydride ring. In addition, according to the infrared spectrum, there is no primary aminogroup in the product (1).

In the PMR spectrum (Fig. 2) that was obtained on the spectrometer “Bruker” (100 MHz), the three main signal groups were found: two unequal signals at the 1.25 and 1.3 ppm with the ratio of the intensities 1:10, fuzzy multiplet in the area of the 4.5–5.2 ppm and singlet at the 7.16 ppm. The last signal undoubtedly is linked to the benzene ring.
protons of the 2,6-di-tert-Butylphenol fragment. Multiplet signal is mainly caused by the methylene groups. Intensity ratio shows that for one substituted phenyl ring there are three methylene groups. Thus, on the basis of the chemical and spectral data, it can be supposed that the product (1) consists of at least two compounds indicated in Fig. 1 as (1a) and (1b).

The product (2) is the low-melting yellow crystalline substance that is well soluble in the benzene. The simplest empirical formula C_{43}H_{65}N_{2}O_{(3–5)}S_{3} was calculated by the average values of the elemental analysis (C – 65.3 %, H – 8.4 %, N – 4.0 %, S – 12.3 %) according to the assumption that all three sulfur atoms of the Xanthane Hydride remain in the product (2). In the Infrared spectrum of the product, there are no absorption bands at the 1640 і 1510 cm\(^{-1}\), that are specific to the Xanthane Hydride ring. On the other hand, in the product (2) there is a band at the 3670 cm\(^{-1}\), that can be attributed to the valent fluctuation of the ОН bond.

In the PMR spectrum (Fig. 3), there are three main groups of signals: signals of the tert-Butyl groups at the 1.18; 1.28; 1.42 ppm with the ratio of the intensities 1:1.5:20, complex multiplet at the area of the 3.6–5.4 ppm, which can be attributed to the CH\(_2\)-groups and –OH, singlet at the 7.16 ppm that is caused by the protons of the substituted phenyl ring. Comparison of the signal intensity of the second and third groups shows that at the every residue of the 2,6-di-tert-Butylphenol there is no more than one methylene group. Consequently, the product (2) is a mixture of the compounds with a clear predominance of the substances formed by condensation of the Xanthane Hydride, 2,6-di-tert-Butylphenol and paraformaldehyde at the ratio 1:3:3 (Fig. 4).

When 3 residues of the 2,6-di-tert-Butylphenol are input, the Xanthane Hydride ring is probably broken by the most labile bond S–S. Quite a high solubility of the product (2) in the non-polar solvents is caused by the presence of the lipophilic residues of the 2,6-di-tert-Butylphenol and also by the fact that Xanthane Hydride ring is split. The results of the investigation of the product (2) in the oil M-11 compared to the TTS and to the industrial additives – high-temperature ashless oxidation inhibitor Borin, zinc dialkyldithiophosphate DF-11 and the additive Irganox 565 (2-(3,5-di-tert-Butyl)-4-hydroxyanilino)-4,6-bis-(n-octylthio)-1,3,5-triazine) are shown in Table 3.

<table>
<thead>
<tr>
<th>№</th>
<th>Characteristics</th>
<th>The value of the characteristics</th>
<th>The method of testing, GOST</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Additive (2)</td>
<td>TTS</td>
</tr>
<tr>
<td>1</td>
<td>Thermal-oxidative stability, 250 °С, minute</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>Oxidation in the device DK-2, 200 °С. Precipitate for 40 hours of the oxidation, % mass</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>Oxidation of the vaseline-oil, 200 °С Induction period, minute</td>
<td>150</td>
<td>140</td>
</tr>
<tr>
<td>4</td>
<td>Corrosion on Pb, 140 °С, 25 hours, g/m(^2)</td>
<td>Absence</td>
<td>4.9</td>
</tr>
<tr>
<td>5</td>
<td>Corrosion on Cu, 120 °С, 3 hours, points</td>
<td>1а</td>
<td>1а</td>
</tr>
</tbody>
</table>

Table 3

The results of the investigation of the oil M-11 with some additives (the additives concentration is 0.5 %; and for Borin it is 1 %)

![Fig. 2. The PMR spectrum of the product (1)](image1)

![Fig. 3. The PMR spectrum of the product (2)](image2)

![Fig. 4. The chemical formulae of the product (2)](image3)
So, according to the results of the experiments, it was found that all investigated additives are almost equivalent in the field of the oil protection from oxidation in the thin layer (250 °C) and corrosion protection on copper. However, the product (2) protects the oil from the oxidation in the volume (200 °C) better than other additives and does not cause corrosion of lead.

5. Conclusions

1. It was found that condensation of the Xanthane Hydride with 2,6-di-tert-Butylphenol(2,6-DTBP) and paraformaldehyde in the glacial acetic acid at the temperature of the 40–45 °C leads to the formation of the complex mixture of the products with the empirical formula C₁₀H₁₂N₂O₃S₃ and the empirical formula C₄₃H₆₅N₂O(3−5)Sₐ.

2. On the basis of the conducted investigations, it was shown that alkylphenol derivatives of the thiocyanic acid and Xanthane Hydride are perspective additives – inhibitors of the corrosion and oxidation of the fuels and lubricants.

3. The technique of the 5-amino-1,2,4-dithiazole-3-thione (Xanthane Hydride) synthesis was improved. It was shown that replacing of the sulfuric acid with the hydrochloric acid has less pressure on the environment and allows to synthesize a product that can be easier purified. An assumption about the structure of the synthesized compounds was set up with the help of the chemical and spectral analyses of the reaction products.

For the compound with the empirical formula C₁₀H₁₂N₂O₃S₃ the structure containing a residue of the 2,6-di-tert-Butylphenol and one heterocyclic fragment was proposed. And for the compound with the empirical formula C₄₃H₆₅N₂O(3−5)Sₐ the structure containing three residues of the 2,6-di-tert-Butylphenol was proposed.

References


1. Introduction

The number of studies of new promising materials based on natural polymers has increased significantly lately, in particular cellulose, which is related to economic and ecological necessity of replacing natural exhaustible sources of carbohydrates (oil, coal) to renewable plant raw materials. Due to its valuable properties, cellulose successfully finds its application not only in paper industry but in other industrial areas, such as chemical, food, pharmaceutical, cosmetic. One of the most promising products of cellulose chemical processing is the microcrystalline cellulose (MCC), which has high content of the ordered part of cellulose with crystallographic orientation of the macromolecules [1, 2], the maximum degree of crystallinity, high density and specific surface [3].

MCC is characterized by chemical resistance, insolvability in water and organic solvents, absence of taste, smell and color that allow using it as a filler, stabilizer and emulsifier in food processing, cosmetic and pharmaceutical industries [4].

The main raw material for obtaining microcrystalline cellulose remains high-quality cellulose produced from wood and cotton. The countries that have no available stocks of wood and cotton as the resources of fibers for obtaining MCC, can consider non-wood plant raw materials, such as bast plants, which have more homogeneous long cells, such as fibers of flax, hemp, kenaf [5].

One of the most profitable crops among those plants in Ukraine remains hemp. Favorable weather conditions, a large reserve of fertile lands, existing human and industrial potential promote the cultivation of hemp in Ukraine. Taking into account that a hectare of hemp produces the weight gain of 6 m³ per year, while deciduous trees do only up to 3.2 m³, the change of wood to hemp during the processing of cellulose is considered advisable economically and ecologically as well [6].

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DEVELOPMENT THE TECHNOLOGY OF OBTAINING MICROCRYSTALLINE CELLULOSE FROM THE HEMP FIBERS

V. Barbash
PhD, Associate Professor*
E-mail: v.barbash@kpi.ua

M. Karakutsa*
E-mail: mary-skies@yandex.ua

I. Trembus
PhD, Associate Professor*
E-mail: lanos0790@yandex.ru

O. Yaschenko
Postgraduate Student*
E-mail: voliav@ukr.net

*Department of ecology and plant polymer technologies
National Technical University of Ukraine
“Kyiv Polytechnic Institute”
Peremohy ave., 37, Kyiv, Ukraine, 03056

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